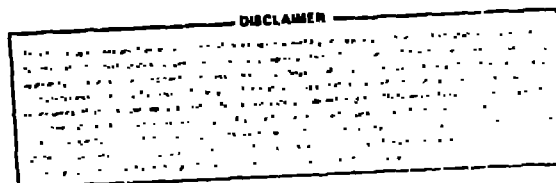$C C N F - 8 o o 6 1 3 7 - -1$

TITLE: PULSE-PROBE MEASUREMENTS IN LOW-TEMEPRATURE, LOW-PRESSURE SF$_6$

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MASTER

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PULSE-PROBE MEASUREMENTS IN LOW-TEMPERATURE, LOW-PRESSURE SF_6 [*]

by

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ABSTRACT

To improve understanding of multiple-photon absorption by polyatomic
molecules, we have performed a series of experiments wherein a pulsed
CO_2 laser irradiated 0.02 to 0.08 torr samples of SF_6 at 145 K. A cw probe
laser monitored the time response of the induced absorption or transmission
at many CO_2 laser lines that are in or near the ν_3 absorption of SF_6.
The experiments covered a 40-fold fluence range and probe times out to
4 ms. We conclude that the absorbed laser radiation produces a nonthermal
vibrational-energy distribution and that intermolecular vibrational-
energy transfer is important at early times in redistributing the
absorbed energy. We also discuss the influence of other processes
on the induced spectrum.

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LOW-PRESSURE SF$_6$

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INTRODUCTION

The experimental determination of the intramolecular distribution of vibrational energy following infrared laser excitation of polyatomic molecules has been a goal of many researchers in recent years. One popular method of investigation has been the pulse-probe technique with SF$_6$ and similar species.

This paper reviews some of our own work with SF$_6$ (Ref. 1 gives a more complete account) and gives some general conclusions about the kind of information these experiments can give.

We performed our experiments at low temperature (145 K) and pressure (0.02 to 0.08 torr) and with a 30-fold laser fluence range (0.018 to 0.54 J/cm^2). The probe laser covered the frequency range of the SF$_6$, ν_3 absorption band. The procedure we used gave a fairly complete mapping of the induced spectrum of this species for a variety of experimental conditions.

Our experiments extend and, in many respects, compliment earlier work (see Refs. 2-7 and others cited in Ref. 1). Several observations were common to all experiments such as the anharmonic shift of the induced spectrum to lower frequencies. However, the investigators do not agree on several mechanistic conclusions from their experiments, such as the time scale for collisionless intramolecular vibrational-energy randomization and the role of intermolecular vibrational-energy transfer.

EXPERIMENTAL

We show a diagram of the apparatus used in these experiments in Fig. 1. A sample of cold, low-pressure SF_6 was irradiated with a pulsed CO_2 laser while monitoring the intensity of the cw CO_2 probe laser after it passed through the irradiated region. A transient digitizer-minicomputer processed the det   r signals and temporarily stored them.
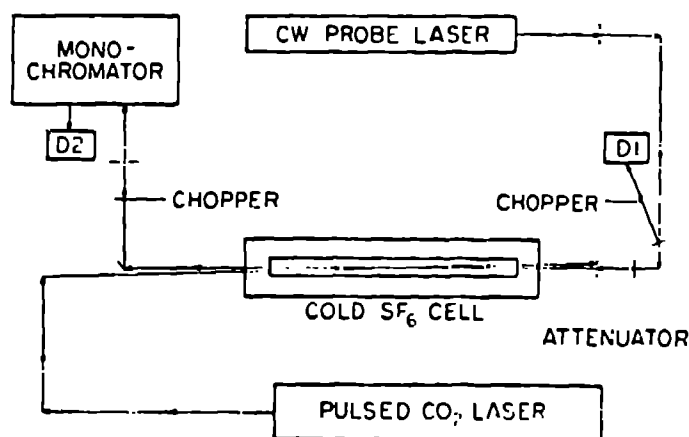

Fig. 1. Apparatus diagram for pulse-probe experiments.

The cold SF_6 absorption cell was a 1.00-m-long by 2.54-cm-id cylinder with CsI windows that contained the SF_6 gas sample. A cooling jacket surrounded this cylinder, and a cylindrical vacuum jacket with KCl windows enclosed the inner cylinder and cooling jacket. The cell temperature was 145 ± 3 K for all experiments.

We operated the pulsed CO_2 laser with a He-CO_2 gas mixture (no N_2) that gave multimode pulses (180 ns FWHM) with no long "tail". An intracavity iris and long focal-length mirrors controlled the spatial profile of the beam at the absorption cell. Pulse energies were lowered by attenuating the beam with a set of partially-reflecting germanium flats that had antireflection coatings on one side. The pulse energy was reproducible to ±5%. Table 1 gives average amount of energy absorbed per molecule at the fluences and pressures we used in our experiments.

The probe laser was a line-tunable cw CO_2 laser equipped with Invar stabilizing rods and piezo-electric control of the cavity length. The latter feature allowed us to tune the laser across the gain profile of a single CO_2 laser line ($\sim$120 MHz).

Table 1. Fluence (Φ) and Energy Absorbed per molecule (η), Averaged Along Probe Path

Φ (J/cm^2)	η		
	0.08 torr	0.04 torr	0.02 torr
0.54	3.7	2.7	2.2
0.19	1.4	1.1	0.89
0.048	0.42	0.33	0.29
0.016	0.15	0.13	0.11

The laser power was about 0.1 W at the absorption cell. The beam was a few millimeters in diameter, yielding an intensity of about 1 W/cm^2 near the beam center.

Detectors D1 and D2 were HgCdTe photovoltaic infrared detectors (SAT) with the total circuit-response time estimated to be 20 ns. D1 was used to keep the laser power and frequency stable and both detectors were employed to take absorption spectra over the laser gain band. For the pulse-probe experiments a Tektronix R7912 Transient Digitizer took the signal from detector D2 for the time period shortly before, during, and after the laser pulse, and digitized and stored the trace. The monochromator was used with all experiments having delay times shorter than 5 ns, to discriminate effectively against the pulsed laser radiation at short time.

The pulse and probe beams crossed within the absorption cell. We attempted to keep the beam geometry the same for all experiments. The centers of the two beams were 0.50 cm apart at the entrance and exit windows of the inner cylinder of the absorption cell and the radial profile of the pulsed beam was very nearly Gaussian with a radius parameter of 0.50 cm.

EXPERIMENTAL RESULTS

Reference 1 gives the procedures for converting the primary data to graphs of absorption cross section vs time or frequency. In Figs. 2-6, we show examples of these graphs. The curves cover the time period during and shortly after the pump-laser pulse for a variety of experimental conditions (see Table 1). They show that pump fluence, SF$_6$ pressure, and probe-laser frequency all have a major effect on the probe signals.

The "on line", "off line" labels in Figs. 3 and 4 refer to the frequency of the probe laser relative to strong absorption
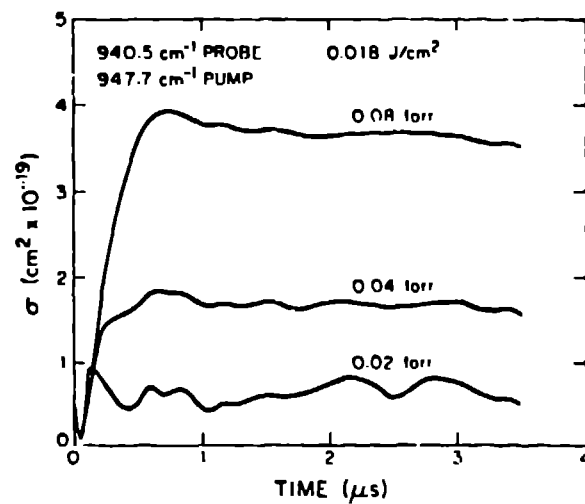
Fig. 2. Absorption cross section vs time for SF_6 at 145 K.
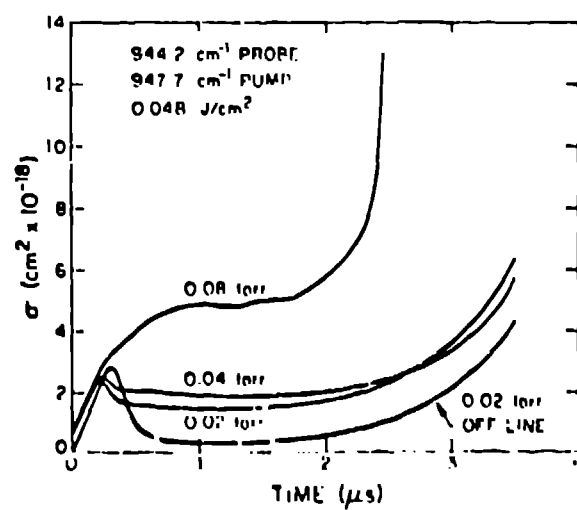

Fig. 3. Absorption cross section vs time for SF_6 at 145 K. The upper three curves are all "on line".
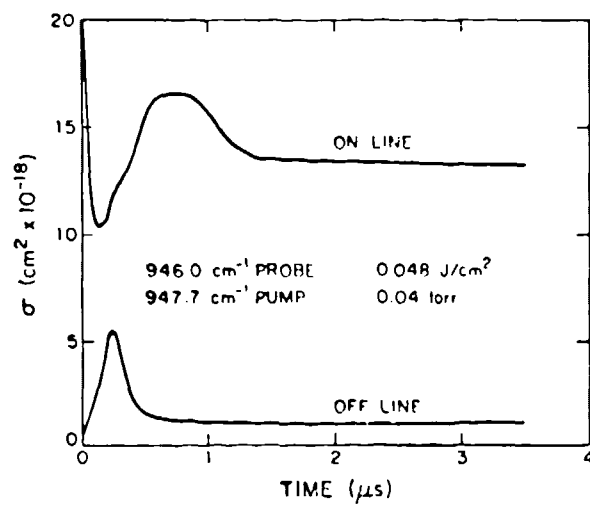
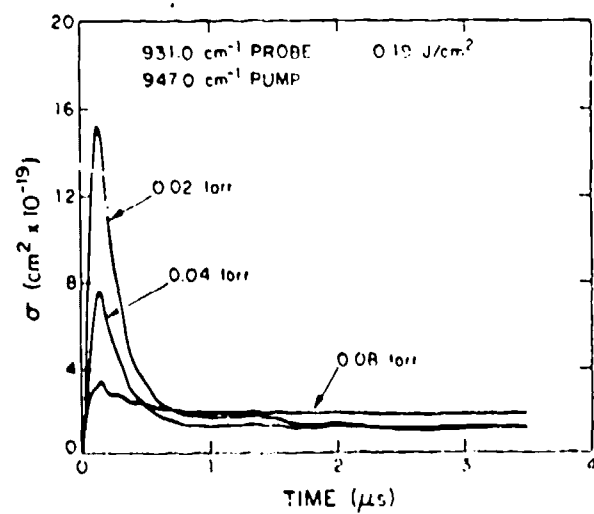Fig. 4. Absorption cross section vs time for SF_6 at 145 K.

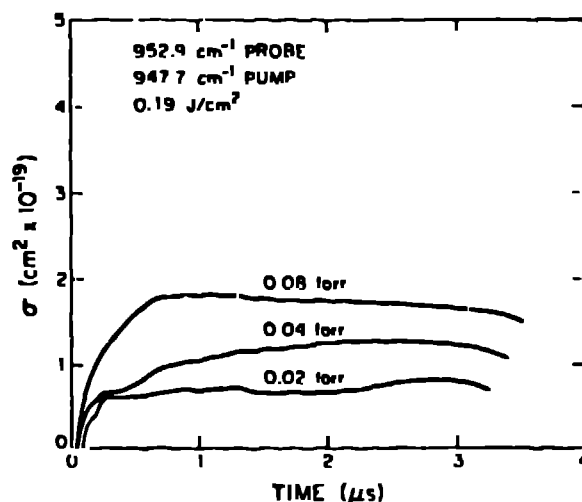Fig. 5. Absorption cross section vs time for SF_6 at 145 K.

Fig. 6. Absorption cross section vs time for SF_6 at 145 K.

features. The frequency difference between the "on line" and "off line" curves is about 25 MHz. From the pulse-probe data, one can also construct composite spectra at different times for various experimental conditions. Figures 7-9 give examples of these composite spectra.

In Fig. 7, we see the evolution of the spectrum during and shortly after the laser pulse for the highest fluence and pressure we employed. Straight lines connect all data points in this and subsequent figures. The large feature in the unexcited spectrum ($t = 0$) is due to $^{32}SF_6$, and the smaller feature is due to $^{34}SF_6$. The thermal spectrum is for the vibrational temperature one obtains (670 K in this case) from a thermal distribution of the absorbed energy among the vibrational degrees of freedom. In Fig. 8 we show spectra for several fluences at 0.40 µs, which is at the end of the exciting pulse.

The induced spectrum of this band relaxes back to the original 145 K spectrum over a very long time period. Figure 9 shows spectra at various times during that relaxation period after irradiation with an average fluence of 0.54 J/cm^2.

DISCUSSION

We make some qualitative . ervations and conclusions about these data and those data others have obtained. Many phenomena
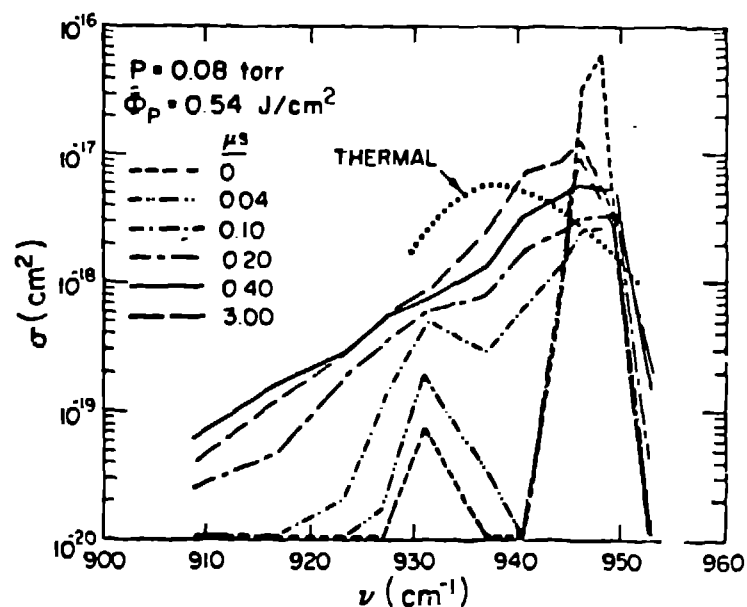
Fig. 7. Absorption cross section vs frequency at successive
times after the beginning of the laser pulse. The
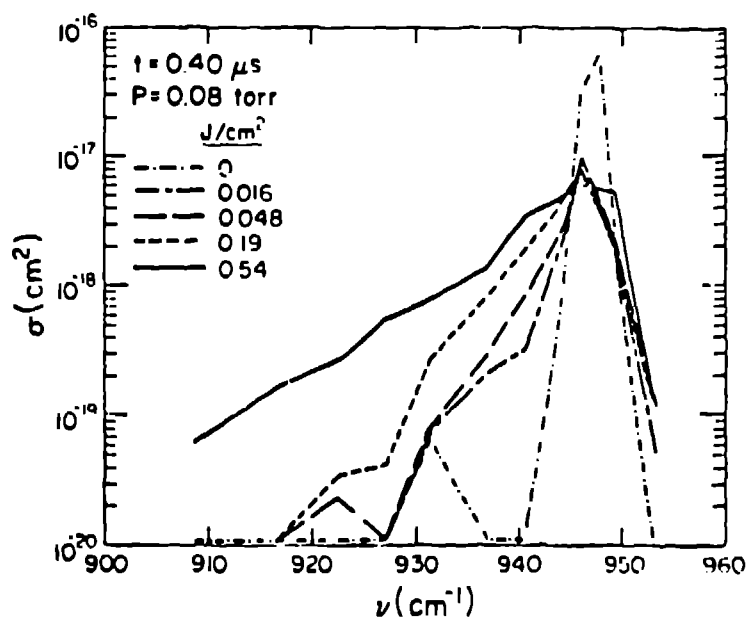thermal spectrum is from Ref. 8 (670 K).

Fig. 8. Absorption cross section vs frequency near the end of
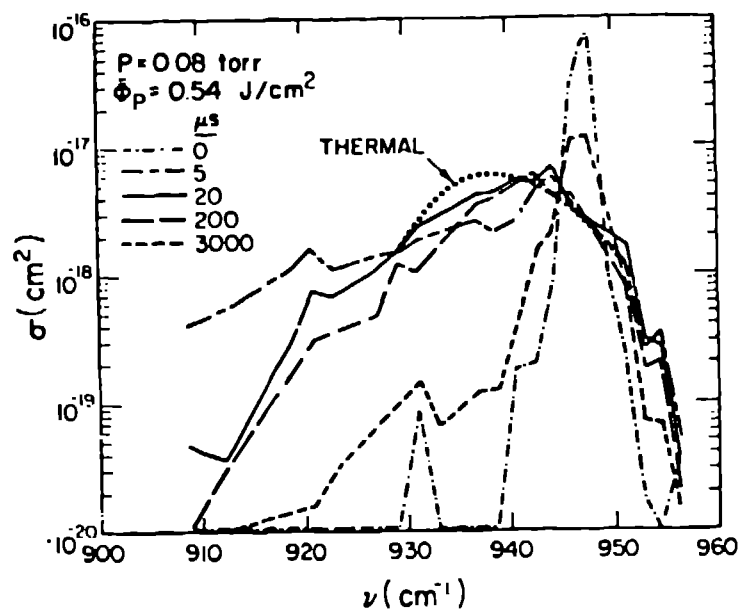the laser pulse for different fluences.

Fig. 9. Absorption cross section vs frequency at successive
times after the beginning of the laser pulse. The
temperature for the thermal spectrum is 670 K.

can and do contribute to the observed probe signals. Let us con-
sider some of them.

For our conditions of low temperature, low pressure, and
high SF_6 oscillator strength, saturation of a given transition
probe laser could occur well below 1 mW/cm^2. The saturation
intensity will, of course, depend on the frequency of the probe
laser. Where the cross section is low, the saturation intensity
is higher. The probe intensity in our experiments was on the
order of 1.0 W/cm^2. Therefore, we should expect to see effects
of probe-laser saturation in our experiments.

For times before or well after perturbation by the pulse
laser, the rate of absorption of energy from the probe beam
approaches a steady state. Because collisional processes such as
rotational relaxation, velocity changing collisions, and power
broadening all enhance that absorption rate, one would expect the
measured probe laser absorption cross section in the steady-state
regions to increase with pressure for the frequencies that do
saturate.

We see this evidence of probe laser saturation in the experiments. In Figs. 2, 3, and 6 we see a monotonic increase of absorption cross section with pressure at times beyond 1 μs. There are, of course, other pressure dependent effects in this time period. Saturation effects play some role in the absorption process, but we should not attribute all pressure effects to saturation.

The pump laser will perturb the probe laser's steady-state absorption rate. It may preferentially excite either the upper level or the lower level of the probe laser transition, and it may excite other species whose subsequent spectrum has a higher absorption cross section at the probe frequency. After perturbation by the pulsed laser, the time necessary to return the levels coupled by the probe laser to a steady-state rate could be shorter than the pulse length for some frequencies. We may see a transient absorption if the pump laser depletes the upper of two levels connected by the probe, or a transient transparency if the pump laser depletes the lower level. The net change in probe-laser absorption cross section before and after the laser pulse is a measure of the change of population of species that interact with the probe frequency.

The transient signals we see in the first 0.5 μs in Figs. 3, 4, and 5 could be due to the pump laser depletion of the levels connected by the probe laser. This effect should give larger signals at lower pressure as we see in Figs. 3 and 5; and it should give positive transients (i.e., increased absorption cross section) at the "off line" frequencies as we see in Figs. 3 and 4.

Another effect that probably contributes to the transient signals during the pump pulse is Rabi splitting of levels that are at or near the energy of the upper or lower probe levels.[6] If, for example, the pump laser is the right frequency to couple the upper probe level with a higher one, the resulting Rabi splitting will produce a transient absorption in the wings of a line and a transient transmission near the line center. This is precisely what we see in Fig. 4.

The effects we have discussed here are relevant to other experiments as well. The conditions for Deutsch and Bruecks's experiments[2,3] were similar to ours. They also saw transient absorption signals similar to Fig. 5. Kwok and Yablonowitch[5] observed rapid transient absorption during much shorter (30 ps) pulses. In both of these experiments the effects we discussed could have contributed to the observations.

Rotational relaxation processes could modify the induced spectrum in two ways: First, by contributing to the amount of

pulse laser energy absorbed by the sample; and second by modifying the rotational energy distribution (and hence, the induced spectrum) during as well as after the laser pulse. Table 1 shows that the amount of absorbed laser energy increases with pressure. A major contribution to this effect is the feeding of molecules by rotational relaxation processes into states that have high absorption rates. This effect can be quite large, even for pressures that are as low as the ones we used in these experiments.[9] The pressure trend we see in Figs. 2 and 3 may be influenced by this increase of absorbed energy with pressure as well as by the saturation effect we discussed above. The relaxation time for the process that Moulton, et al.[6] attribute to rotational energy redistribution is 36-ns-torr for SF_6 at room temperature. A correction for collision rate alters this time to 25-ns torr at the temperature of our experiments, 145 K. This gives rotational-relaxation times of 300 ns at 0.08 torr. The broadening of the spectrum to higher frequency with time during and shortly after the pulse (Fig. 7) is probably due to collisional excitation of higher energy-rotational states.

It will be difficult for us to determine the rate of collisionless, intramolecular V-V energy transfer. Many experimenters[2,3,5,10] have attempted to measure the rate of this elusive process in SF_6, and the times they have reported differ by many decades. We would be able to observe changes in the spectrum from this process only if they would occur on a time scale on the order of the laser pulse length. If the time scale for the process were shorter than the pulse length, the changes in the spectrum would tend to follow the pulse, and if it were much longer than the pulse length, collisional processes would dominate. A detailed analysis of the induced spectrum could perhaps determine whether or not the absorbed energy remained for any length of time in the normal mode. Until recently the indications were that vibrational excitation in the ν_3 normal mode would give a much greater anharmonic frequency shift than the same amount of vibrational energy statistically distributed among all normal modes of the molecule. (See, for example, the analyses in Refs. 2 and 3). The recent analysis[11] of the $3\nu_3$ overtone band of SF_6 indicates that this is not so. The anharmonicity constant, X_{33}, is about half of the previous estimate.[12] The effects of anharmonic splitting within the ν_3 mode are greater than the small differences between (1) the anharmonic shifts due to excitation in the ν_3 mode and (2) those from a statistical distribution of the same energy among all modes.[8,12] This reevaluation of X_{33} clouds the interpretations others[3,4,16] have made about intramolecular vibrational energy transfer.

Because of these spectroscopic reasons it will also be difficult to diagnose the effect of <u>collisional</u> intramolecular

V-V energy transfer. If the collisionless process were rapid, and if it produced a random intra-molecular energy distribution, the collisional process would play no role.

The case for extracting intermolecular V-V energy-transfer information from the pulse-probe experiments is better. It is clear from many experiments, including those we report here, that the vibrational-energy distribution that a pulsed-CO_2 laser produces in low pressure SF_6 is one that deviates significantly from a thermal distribution. The frequency shift of the spectrum is roughly proportional to the amount of vibrational energy.[8] Intermolecular V-V energy-transfer processes drive the population from the initial nonequilibrium distribution towards one describable by a single vibrational temperature. For example, we see in Fig. 7 that changes in the spectrum occur between 0.4 µs and 2.0 µs that are consistent with the redistribution of the available vibrational energy. We see similar changes between the 5 and 20 µs in Fig. 9. Over this time period the low-frequency tail and the band center portion of these spectra fall, while the intermediate portion rises and the peak of the spectra shift to lower frequencies. Thus, the 20 µs spectrum is much nearer the thermal spectrum. One would expect some changes on this time scale since the mean time between gas-kinetic collisions is about 1 µs at 0.06 torr. These changes are consistent with de-excitation of high-energy species along with excitation of lower-energy species, i.e., intermolecular V-V energy transfer. Bates, et. al.[13] give 1.5 µs-torr for an intermolecular V-V relaxation time in room temperature SF_6. This translates to 1.0 µs-torr for our temperature. This is consistent with the relaxation time we derived from our experiments of 1-2 µs-torr.

Deutsch and Brueck[2],[3] observed similar changes in the induced spectrum of SF_6 at room temperature. They interpreted the changes to be due to collisionless intramolecular energy redistribution. We feel, however, that a more consistent interpretation of their data is the same intermolecular energy transfer processes that we are postulating for our experiments. The "collisionless" nature of their relaxation times is an artifact of the data reduction method they used.

Fuss and Hartmann[4] observed some structure in their pulse-probe spectra that they attributed to two- and three-photon resonances. We would expect to see less of this effect in our experiments because our pump frequency was at the peak of the one-photon spectrum. The major multiphoton resonances occur at lower frequencies.[13,14]

There are two other processes that could influence the induced spectra after long delay times. These are V-T transfer

and diffusion. The latter dominates the spectra beyond a few hundred microseconds (Fig. 9) and the former is too slow[7] to have more than a minor effect.

CONCLUSIONS

In these experiments we found that for some frequencies saturation of the probe transitions alters the probe signals. These saturation effects, along with Rabi splitting of states by the pulsed laser, produce rapid transient signals for some probe frequencies.

The experiments indicate that the initial distribution of absorbed laser radiation in a low pressure, low temperature SF_6 sample is not thermal. The laser tends to produce more highly excited molecules and to leave more unexcited molecules than would be the case for a thermal distribution.

Rotational energy transfer also plays an important role in the absorption and redistribution of laser radiation. This process is particularly important during the laser pulse.

The preliminary analysis of the pulse-probe data gave little information about the intramolecular distribution of absorbed laser radiation or the (collisionless) rate of approach of that distribution to a statistical one. Understanding the extent and rate of intramolecular randomization of vibrational energy would require a more thorough analysis, and perhaps, independent experiments.

We feel that intermolecular vibration-to-vibration energy transfer contributes significantly to the relaxation of that energy for our conditions. We estimated this V-V relaxation time to by 1-2-μs torr in systems that do not deviate significantly from equilibrium.

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